FORMATION AND STABILITY OF METHANE HYDRATES IN CLAY INTERLAYERS

Sung-Ho Park, Garrison Sposito, Rebecca Sutton and Jeffery A. Greathouse

Contact: Sung-Ho Park, 510/643-9951, sungho_park@lbl.gov

RESEARCH OBJECTIVES

The objectives of this project are to: (1) evaluate whether methane hydrates can form in hydrated 2:1 clay interlayers; (2) determine optimal conditions for hydrate formation of this kind, in terms of pressure, temperature and methane concentration; and (3) estimate the stability of the interlayer clathrate in terms of the translational motions of methane.

APPROACH

Our approach uses computer simulations based on Monte Carlo (MC) and molecular dynamics (MD) methods. Natural methane hydrates are found where marine sediments, including 2:1 clay minerals, are also found. Therefore, modeling was initiated by Monte Carlo phase-sampling of a system containing not only methane and water molecules, but also the clay mineral Na-montmorillonite. Our laboratory is well-experienced in the study of water structure in restricted geometry, especially within the clay interlayers. After finding a clathrate structure (20 to 22 methane-oxygen coordination number) from MC simulations, we carried out MD simulations to study its stability and dynamical properties.
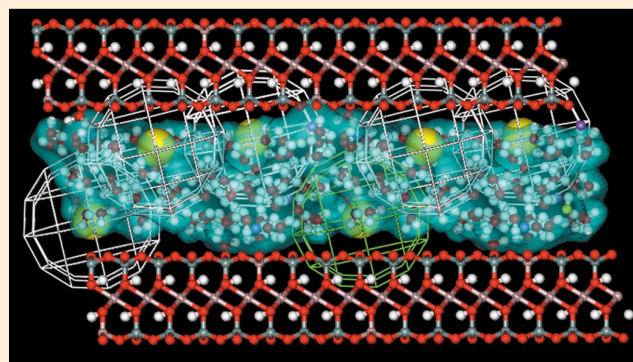

Figure 1. Monte Carlo "snapshot" of methane hydrates in a Na-montmorillonite interlayer. The "cage" indicates methane clathrate formation between water oxygens and oxygens from the clay mineral surface. The cage volume includes oxygens within 5.5 Å of the methane molecule.

ACCOMPLISHMENTS

From the MC simulations, the most stable structures observed were at atmospheric pressures of 10, 20 and 30 for a three-layer hydrate of Na-montmorillonite containing 0.5, 1.0, or 2.25 methane molecules per clay unit cell, respectively. The first two methane systems showed 22- and 20- coordination of methane with oxygens from both the clay surface and interlayer water molecules (Figure 1). The third system showed methane molecules in close proximity to each other, indicating possible phase separation. In our MD simulations, the first two systems showed relatively low methane self-diffusion coefficients in comparison with the third system. Clathrate-like behavior also was observed for the first two methane systems with respect to their velocity autocorrelation functions (VACFs) for methane. The power spectrum, obtained through Fourier transform of the VACF, is consistent with published inelastic incoherent neutron scattering data on methane hydrates in pure water alone. Pair correlations in terms of radial distribution functions, power spectra, VACFs and the self-diffusion coefficients of methane and water all indicated a clathrate-like structure of the methane hydrate in clay interlayers for both of the lower-concentration methane systems. The highest-concentration methane system did not show a stable clathrate structure.

SIGNIFICANCE OF FINDINGS

The new clathrate structure proposed for hydrated clay interlayers is important for understanding the formation and stability of natural gas hydrates. Our modeling may give valuable insight for future studies of methane hydrate P/T relations.

RELATED PUBLICATIONS

Sposito, G., N.T. Skipper, R. Sutton, S.-H. Park, A.K. Soper and J. Greathouse, Surface geochemistry of the clay minerals, Proc. Natl. Acad. Sci. USA 96: 3358, Berkeley Lab report LBNL-43158, 1999.

Sposito G., S.-H. Park and R. Sutton, Monte Carlo simulation of the total radial distribution function for interlayer water in sodium and potassium montmorillonites, Clays Clay Miner, 47: 192, Berkeley Lab report LBNL-42847, 1999.

Park, S.-H., and G. Sposito, Monte Carlo simulation of total radial distribution functions for interlayer water in Li-, Na-, and K-montmorillonite hydrates, J. Phys. Chem. B, 104: 4642, Berkeley Lab report LBNL-45842, 2000.

ACKNOWLEDGEMENTS